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Communications

Novel Dimeric Organotin Cations: Highly Effective Alcohol Acetylation Catalysts

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Summary: Novel organotin cations, $[R_2SnOH(H_2O)]_2^{2+}(OTf)^-_2$ ($R = n$-Bu and t-Bu), were prepared from R_2SnO and CF_3SO_3H (TfOH). The synthetic utility of these compounds due to the increased Lewis acidity was exemplified by their high catalytic activity in the acetylation of alcohols.

The development of organotin cations is synthetically significant with regard to increasing the Lewis acidity of inherently weak acidic organotin compounds. Despite their long history,[1] however, only a limited number of the cationic compounds have been isolated. The trimethyltin cation hydrates[2] and ammoniates[3] have been known since the 1960s, whereas diorganotin dications stabilized by internal coordination with alkynylborates were reported recently.[4] The tin cluster dications $[(RSn)_{12}O_{14}(OH)_6]^{2+}$ were also produced and fully characterized.[5] In the course of our project on the synthetic applications of organotin Lewis acids, we have prepared novel organotin dications, $(R_2SnOH)_2^{2+}(OTf)^-_2$ ($Tf = CF_3SO_2$), which exhibit high catalytic activity in the acetylation of alcohols, as expected on the basis of their increased Lewis acidity.

We attempted to prepare 1,3-bis(triflato)distannoxane **2** by treating $(ClBu_2SnOSnBu_2Cl)_2$[6] with AgOTf in toluene, but $[Bu_2Sn(OH)(OTf)(H_2O)]_2$ (**1a**) was, in fact, isolated (Scheme 1). Probably, **2** underwent facile hydrolysis and coordination by H_2O even when only a trace amount of water was present in the solvent, because the tin atoms in **2** are highly electrophilic due to bonding to the electronegative triflato group. In consideration of this reaction path, we designed a simpler route to **1a**, the hydrolysis of $Bu_2Sn(OTf)_2$, which can be readily obtained from Bu_2SnCl_2 and AgOTf.[7] Even more conveniently, direct reaction of Bu_2SnO with TfOH furnished **1a** in 98% yield.[8] The *tert*-butyl derivative **1b** was prepared from *t*-Bu_2SnO and TfOH as well.[9] These compounds are stable in air and lose the coordinated

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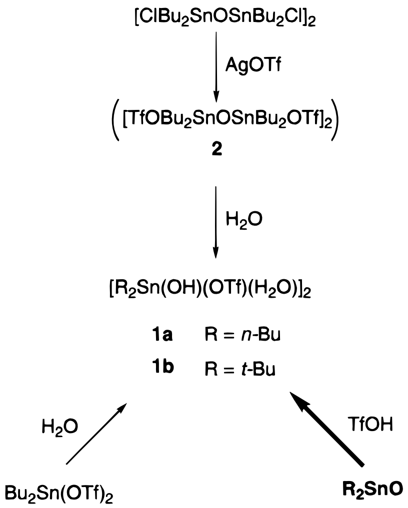
Scheme 1



H_2O molecules at 25 °C in vacuo over several days to form the nonhydrated species.

Figure 1 illustrates the structure of **1a** determined by single-crystal X-ray analysis.[10] The molecule is dimeric with hydroxyl bridges, and each tin atom is six-coordinated. Analogous dimeric structures, but without hydration, have been reported for $[t\text{-}Bu_2Sn(OH)Cl]_2$ (**3**)[11] and $[Me_2Sn(OH)NO_3]_2$.[12] We also prepared $[t\text{-}Bu_2Sn(OH)NO_3]_2$ (**4**) by treating $[t\text{-}Bu_2Sn(OH)Cl]_2$ with $AgNO_3$. The structural similarity between **4** and $[Me_2Sn(OH)NO_3]_2$ was confirmed on the basis of their IR spectra in the solid state and a single-crystal X-ray analysis.[13] It should be noted for these compounds that each tin atom is five-coordinated and the Cl and NO_3 substituents are bonded covalently to tin. On the other hand, the interaction between Sn and the triflato ligand in **1a** is very weak since the distance between Sn and the triflato oxygen is 2.622 Å.[14] Thus, this interaction is easily dissociated in solution to generate the dimeric cation species. The ^{119}Sn NMR spectra of **1a** and **1b** in acetone-d_6 exhibited a singlet at −203.2[15] and −249.7 ppm, respectively, diagnostic of five-coordinate tin.[16] The formation of the ionic species was further confirmed by electrical conductivity measurements (Table 1). The ionic dissociation of both **1a** and **1b** in acetonitrile solution is evident from the large conductivity values.[17] In contrast, **3** proved to be almost a nonelectrolyte and **4** was a weak electrolyte.

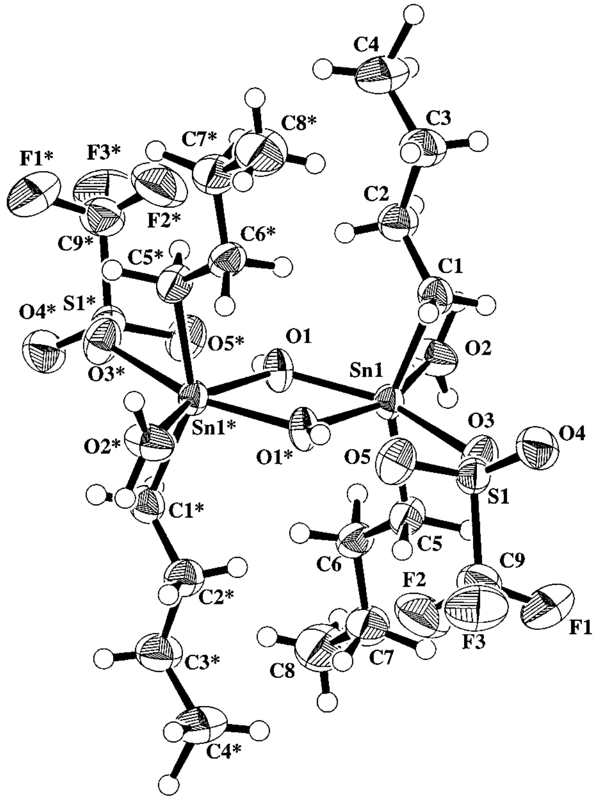


Figure 1. ORTEP view of **1a**. The thermal ellipsoids are drawn at the 50% probability level. Selected bond distances (Å) and angles (deg): Sn1−O1 = 2.085(3), Sn1−O1* = 2.147(3), Sn1−O2 = 2.409(3), Sn1−O3 = 2.622(4), Sn1−C1 = 2.137(5), Sn1−C5 = 2.119(5), S1−O3 = 1.459(4), S1−O4 = 1.430(4), S1−O5 = 1.443(4); O1−Sn1−O1* = 71.0(1), O1−Sn1−O2 = 84.4(1), O1−Sn−O3 = 150.6(1), O1*-Sn1−O2 = 155.4(1), O1*-Sn1−O3 = 79.6(1), O2−Sn1−O3 = 125.0(1), O1−Sn1−C1 = 104.0(2), O1−Sn1−C5 = 104.7(2), O1*-Sn1−C1 = 100.0(1), O1*-Sn1−C5 = 98.9(2), O2−Sn1−C1 = 87.2(1), O2−Sn1−C5 = 85.4(2), C1−Sn1−C5 = 149.5(2), Sn1−O1−Sn1* = 109.0(1).

Table 1. Conductivities of Organotin Compounds[a]

	molar conductivity	conductivity/μS cm^{-1}
1a	43.5	870
1b	49.7	994
3	1.8	37
4	12.0	240

[a] In CH_3CN (10 mmol/L).

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(8) A suspension of Bu_2SnO (498 mg, 2.0 mmol) and TfOH (300 mg, 2.0 mmol) in acetonitrile (30 mL) was stirred at room temperature. After 5 h, a clear solution resulted, and filtration followed by evaporation afforded **1a** (782 mg, 98%). ^1H NMR (acetone-d_6): δ 0.85−0.97 (m, 6H), 1.32−1.47 (m, 4H), 1.65−1.95 (m, 8H). ^{13}C NMR (acetone-d_6): δ 13.8 (2C), 13.9 (2C), 27.0 (4C), 27.2 (4C), 27.3 (2C), 27.5 (2C), 120.9 (2C, $J_{C-F} = 319$ Hz). ^{19}F NMR (acetone-d_6): δ −78.1. ^{119}Sn NMR (acetone-d_6): δ −203.2. Anal. Calcd for $C_{18}H_{38}F_6O_8S_2Sn_2$ as the nonhydrated species (recrystallized from CH_2Cl_2 followed by dehydration as described in the text): C, 27.09; H, 4.80. Found: C, 26.88; H, 4.67.

(9) NMR data for **1b**: ^1H NMR (acetone-d_6) δ 1.56 (s); ^{13}C NMR (acetone-d_6) δ 30.0 (6C), 47.8 (2C), 120.7 (2C, $J_{C-F} = 318$ Hz); ^{19}F NMR (acetone-d_6) δ 77.9; ^{119}Sn NMR (acetone-d_6) δ −249.7. Anal. Calcd for $C_{18}H_{38}F_6O_8S_2Sn_2$ as the nonhydrated species: C, 27.09; H, 4.80. Found: C, 26.84; H, 4.73.

(10) Crystallographic data for **1a** ($C_9H_{21}F_3O_5SSn$, 15 °C): triclinic, $P\bar{1}$, $a = 8.727(2)$ Å, $b = 11.685(1)$ Å, $c = 8.1108(5)$ Å, $V = 808.9(2)$ Å^3, $\alpha = 94.210(7)°$, $\beta = 101.20(1)°$, $\gamma = 90.51(2)°$, $Z = 2$, $R = 0.033$, $R_w = 0.059$.

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(13) IR data (NO_3) in Nujol mull: for **4**, 1030, 1280, 1515 cm^{-1}; for $[Me_2Sn(OH)NO_3]_2$, 1000, 1287, 1506 cm^{-1}.[12a] The X-ray analysis of **4** will be reported in a full paper.

(14) The Sn−O distance of 2.802 Å has been taken to be Sn−O bonding: Casa, J. S.; Castellano, E. E.; Condori, F.; Couce, M. D.; Sánchez, A.; Sordo, J.; Valera, J. M.; Zuckerman-Schpector, J. *J. Chem. Soc., Dalton Trans.* **1997**, 4421.

(15) The ^{119}Sn NMR spectrum of **1a** gave rise to two very small signals at −162.6 and −134.0 ppm, respectively. These may be attributable to a higher homologue that was formed by further condensation of **1a**. The details will be discussed in a full paper.

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(17) For an example of an $A^{2+}B^-{}_2$ electrolyte, the molar conductivity of $Cd(ClO_4)_2$ is 112 (10 mmol/L in CH_3CN). See: Janz, G. J.; Tomkins, R. P. T. *Nonaqueous Electrolytes Handbook*; Academic Press: New York, 1972; Vol. 1, p 419.

Table 2. Acetylation of Phenethyl Alcohols[a]

$$\mathrm{ROH} \xrightarrow[30\ ^\circ\mathrm{C}]{\mathrm{Ac_2O/cat}} \mathrm{ROAc}$$

ROH	cat. (conc/mol %)	reacn time	yield/%[b]
$Ph(CH)_2OH$	**1a** (0.01)	10 min	93
	1a (0.005)	30 min	93
	1b (0.01)	10 min	95
	1b (0.005)	30 min	90
	1b (0.001)	4.5 h	89
	3 (0.1)	10 min	4
		24 h	82
	4 (0.1)	10 min	5
		24 h	92
	5 (0.15)	10 min[c]	8
		24 h	43
$PhCH(OH)CH_3$	**1a** (0.01)	10 min	96
	1a (0.005)	30 min	92
	1b (0.01)	10 min	91
	1b (0.005)	30 min	98
	3 (0.1)	24 h	18
	4 (0.1)	24 h	26
	5 (0.15)	24 h	22

[a] Reaction conditions: ROH (5 mmol); Ac_2O (5 mL). [b] Determined by GLC. [c] Yields under similar conditions: 9% (Bu_2SnCl_2), 18% ($Bu_2Sn(OAc)_2$), 7% ($ClBu_2SnOSnBu_2Cl$), 2% (without catalyst).

The consequences in synthetic applications of the increased Lewis acidity of the dications **1** were assessed in terms of the catalytic activity for acetylation of phenethyl alcohols with Ac_2O (Table 2).[18] Remarkably, only *0.005 mol %* concentration of **1a** or **1b** was sufficient to give quantitative yields of the desired acetates at *30 °C after 30 min*, whereas a higher catalyst loading and longer reaction times were necessary when neutral catalysts **3** and **4** were used. Apparently, the catalytic activity is dependent on the ionic dissociation of the catalysts in solution. This was further supported by the poor catalytic activity of a monocationic compound, $[(CH_3)_3Sn(H_2O)_2]^+Ph_4B^-$ (**5**),[2] which was found to be virtually a nonelectrolyte on the basis of conductivity measurements (47 μS cm^{-1} in CH_3CN (10 mmol/L)).

In summary, a novel type of organotin cation dimers have been synthesized. These compounds exhibit high catalytic activity in the acetylation of alcohols. It follows, therefore, that the increase in Lewis acidity gained by generating cationic organotin species should be of great synthetic promise. Studies along these lines are underway in our laboratories.

Acknowledgment. Thanks are due to Professor T. Tominaga at the Okayama University of Science for conductivity measurements.

Supporting Information Available: Text and tables giving X-ray crystal structure data for **1a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(18) For acylation of alcohols by nonionic organotin Lewis acid catalysts, see ref 6 and the references therein.